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**THE REACTIONS OF IRON-CARBONYL AND ALKYNE-CARBONYL COMPLEXES WITH NICKELOCENE,  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$  AND  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{RC}_2\text{R}')$ . CRYSTAL STRUCTURES OF TWO HETEROMETALLIC TETRANUCLEAR CLUSTERS**

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**Summary**

The reaction of nickelocene,  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$  and its alkyne-substituted derivatives with  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_3(\text{CO})_{12}$  and alkyne-cluster derivatives of iron are reported and discussed. A considerable number of new heterometallic complexes has been obtained: the structures of the two tetranuclear complexes  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}_2(\text{CO})_7$  (I) and  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Et}_2)$  (IIa) have been determined by X-ray diffraction methods. Crystals of I are triclinic,  $a$  8.028(8),  $b$  14.561(12),  $c$  7.961(8) Å;  $\alpha$  94.58(7),  $\beta$  97.26(11),  $\gamma$  92.23(9)°; space group  $P\bar{1}$ . Crystals of IIa are triclinic,  $a$  10.124(10),  $b$  14.676(12),  $c$  8.396(8) Å;  $\alpha$  95.80(8),  $\beta$  111.20(10),  $\gamma$  72.89(9)°, space group  $P\bar{1}$ . Both structures have been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to  $R = 0.039$  for I and 0.045 for IIa. The structure of I is characterized by a tetrahedral metal atom core, bound to two cyclopentadienyl ligands (through the Ni atoms) and to six terminal CO's (through the Fe atoms). The seventh carbonyl is triply bridging between two Fe and one Ni atoms in an asymmetric way. The structure of IIa consists of a tetrahedrally distorted square arrangement of two Fe and two Ni atoms. The alkyne is  $\sigma$ -bonded to the Ni atoms and  $\pi$ -bonded to the Fe atoms.

The formation of heterometallic complexes in the above reactions is not selective, although the stability of the cluster reactants, and the nature of the bonding and the substituents in the alkynes can influence the nature and the yields of the products.

## Introduction

Interest in heterometallic clusters has increased in recent years [1], partly because of their potential use in homogeneous catalysis [2].

We have previously synthesized and structurally characterized some iron–nickel and ruthenium–nickel derivatives [3–6]. We now report the results of all the reactions of iron–carbonyl and alkyne–carbonyl complexes with nickelocene,  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$  and  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{RC}_2\text{R}')$  ( $\text{R} = \text{R}' = \text{Ph, Et}$ ;  $\text{R} = \text{H, R}' = \text{t-Bu}$ ) in hydrocarbon solvents.

New tetra- and tri-nuclear heterometallic products were obtained from the above reactions. The preparative methods and the structures of the tetranuclear  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}_2(\text{CO})_7$  (I) and  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Et}_2)$  (IIa) have been investigated in detail. A preliminary account of the crystal structures of these two complexes has been already given [7].

The formation of the tetranuclear and the trinuclear heterometallic derivatives is not strictly selective. The ligand exchange processes between different metals add to the difficulty of understanding the reaction patterns. However it can be shown that type and yield of the products is dependent on the stability of the cluster reactants, on the alkyne substituents, and on the bonding of these substituents to the metals.

Complex I consists of a tetrahedral metal-atom core with six terminal CO groups bonded to the iron atoms; of these, one CO is slightly bent forming an incipient semi-bridge [8]. A triply bridging CO is present, interacting with two iron and one nickel atom; two cyclopentadienyl ligands are coordinated to the nickel atoms.

Complex IIa [3] and its homologues [9] were thought to be “butterfly” derivatives by comparison with the cobalt derivatives; indeed Fe–Ni and Co–Co bonds are isoelectronic, but, in fact, in IIa, a tetrahedrally distorted square arrangement of metal atoms is present. The CO groups are terminally bonded to the iron atoms, and the cyclopentadienyl ligands to the nickel atoms. The alkyne interacts  $\pi$  with the nickel and  $\sigma$  with the iron atoms.

The structures of these complexes differ from those of the tetrametallic carbonyl and alkynecarbonyls of the cobalt triad. This makes it difficult to compare the bonding of the alkyne in related (isoelectronic) metallic systems in view of the activation of the triple bond [10].

## Experimental

*Reactants.* The 3,3-dimethylbut-1-yne was purchased from K&K, the hex-3-yne from Farchan, tolane, triphenylphosphine and triethylphosphite from Fluka, nickelocene from Schuchardt and bis(cyclopentadienylcarbonylnickel) from Alfa-Ventron.  $\text{Fe}_3(\text{CO})_9(\text{RC}_2\text{R})$  ( $\text{R} = \text{Ph}$  [11],  $\text{Et}$  [12]) and  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{RC}_2\text{R}')$  [13,14] were obtained by literature methods. The nickel derivative with  $\text{R} = \text{H}$ ,  $\text{R}' = \text{t-Bu}$ , not previously reported, is a dark-green crystalline product, air sensitive on TLC plates, and stable for some days when stored under nitrogen at  $-10^\circ\text{C}$ .

*Purification of the products.* The considerable number of products from each reaction necessitated the use of TLC plates (Kieselgel P.F. Merck, eluant

mixtures of ethyl ether and light petroleum) for separation, even though some air-sensitive products were lost.

*Analysis of the products.* The complexes were analyzed by use of an F&M 185 C, H, N analyzer and a Perkin—Elmer 303 Atomic Absorption Spectrophotometer; the IR spectra were recorded on a Beckman IR-12 instrument, and the NMR spectra on JEOL C60 HL instrument. The mass spectra were determined with a Hitachi Perkin—Elmer RMU-6H or a Varian CH-5 spectrometer.

The physical properties, analytical data, IR spectra and  $^1\text{H}$  NMR spectra, and relevant mass spectral data for the complexes identified are listed in Table 1.

*Reactions.* Unless otherwise stated, all the reactions were performed in refluxing heptane under dry nitrogen in ordinary laboratory glassware. The reactions and the yields are listed in Scheme 1.

### *X-ray data collection*

An irregular grey crystal of I (with dimensions of ca.  $0.11 \times 0.15 \times 0.26$  mm) and a flat blue-black crystal of IIa (with dimensions of ca.  $0.05 \times 0.15 \times 0.22$  mm) were used for the data collection.

Preliminary cell parameters for both compounds were first determined from rotation and Weissenberg photographs and then refined from a least-squares procedure of  $\theta$  values for 18 (I) and 16 (IIa) reflections accurately measured by single-crystal diffractometry. The more significant crystal data are as follows:  $\text{C}_{17}\text{H}_{10}\text{Fe}_2\text{Ni}_2\text{O}_7$  (I),  $M = 555.38$ , triclinic,  $a$  8.028(8),  $b$  14.561(12),  $c$  7.961(8) Å;  $\alpha$  94.58(7),  $\beta$  97.26(11),  $\gamma$  92.23(9)°;  $V$  919(2) Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calc}}$  2.01 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  36.14 cm<sup>-1</sup>; space group  $P\bar{1}$  (from structure determination).  $\text{C}_{22}\text{H}_{20}\text{Fe}_2\text{Ni}_2\text{O}_6$  (IIa),  $M = 609.51$ , triclinic,  $a$  10.124(10),  $b$  14.676(12),  $c$  8.396(8) Å;  $\alpha$  95.80(8),  $\beta$  111.20(20),  $\gamma$  72.89(9)°;  $V$  1111(2) Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calc}}$  1.821 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  29.94 cm<sup>-1</sup>; space group  $P\bar{1}$  (from structure determination).

Intensity data were collected at room-temperature using a Siemens AED automated single-crystal diffractometer with the Nb-filtered Mo- $K_\alpha$  radiation and the  $\theta$ — $2\theta$  scan technique. 3586 independent reflections were measured for I (with  $\theta$  in the range 3—26°) and 2714 for IIa (with  $\theta$  in the range 3—22°); of these, 2570 for I and 1338 for IIa were labelled as observed, having  $I \geq 2\sigma(I)$ . A standard reflection was periodically measured after every 20 reflections to check the stability of the sample and of the instrument. The intensities were corrected for Lorentz and polarization effects, but no absorption corrections were applied in view of the low absorbance of both samples. The first absolute scale and the mean temperature factor were determined by Wilson's method.

### *Structure determination and refinement*

Both structures were solved by the heavy-atom technique; the refinements were carried out by least-squares full-matrix cycles using the SHELX system of computer programs [15] with initially isotropic and then anisotropic thermal parameters for all the nonhydrogen atoms. The hydrogen atoms were placed at the geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameters. The final conventional  $R$  values were 0.039 (for I) and 0.045 (for IIa) (observed reflections only). The atomic scattering factors used (corrected for the anomalous dispersion of Fe and Ni)

TABLE 1  
ANALYSIS AND INSTRUMENTAL RESULTS FOR THE Fe-Ni COMPLEXES

Complex	Elemental analysis (Found (calcd.) (%))				IR spectrum ( $\text{cm}^{-1}$ , n-heptane)	$^1\text{H}$ NMR ( $\delta$ , ppm)	Mass spectrum <sup>a</sup>	Ref.
	C	H	Fe	O				
(Cp) <sub>2</sub> Ni <sub>2</sub> Fe <sub>2</sub> (CO) <sub>7</sub> (I)	37.01 (36.77)	1.97 (1.81)	20.51 (20.11)	18.93 (20.17)	21.78 (21.14)	4.80s	566 m/e (P <sup>+</sup> ) (Fe <sub>2</sub> Ni <sub>2</sub> )	7
(Cp) <sub>2</sub> Ni <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> E <sub>2</sub> ) (IIa)	43.38 (43.35)	3.46 (3.31)	18.51 (18.33)	15.47 (15.75)	19.18 (19.26)	4.70s (10 H) 6.20-6.60 qq (4 H) 7.20-7.40 tt (6 H)	608 m/e (P <sup>+</sup> ) (Fe <sub>2</sub> Ni <sub>2</sub> )	7
(Cp) <sub>2</sub> Ni <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> Ph <sub>2</sub> ) (IIb)	51.25 (51.07)	2.96 (2.86)	16.01 (16.85)	13.57 (13.60)	16.21 (16.64)	2.50-3.00 m (10 H), 4.75s (10 H)	decomp.	3
Cp <sub>2</sub> Ni <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (HC <sub>2</sub> Me) (IIc)	40.61 (40.22)	2.75 (2.49)	19.51 (19.68)	16.10 (16.92)	21.03 (20.69)	—	566 m/e (P <sup>+</sup> ) (Fe <sub>2</sub> Ni <sub>2</sub> )	this work
(Cp) <sub>2</sub> Ni <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (HC <sub>2</sub> Bu-t) (IIId)	43.01 (43.35)	3.72 (3.36)	18.61 (18.33)	15.66 (15.75)	19.00 (19.26)	b	decomp.	this work
(Cp) <sub>2</sub> Ni <sub>2</sub> Fe <sub>2</sub> (CO) <sub>3</sub> (C <sub>2</sub> Ph <sub>2</sub> ) (IIIa)	57.80 (57.32)	3.78 (3.56)	10.00 (9.78)	7.39 (8.48)	21.02 (20.76)	2.70s (10 H) 4.80s (10 H)	decomp.	9

(Cp) <sub>2</sub> Ni <sub>2</sub> Fe(CO) <sub>3</sub> (C <sub>2</sub> Et) <sub>2</sub> (IIIb)	deep-green solid	49.01 (48.59)	4.71 (4.29)	11.52 (11.89)	9.61 (10.22)	25.15 (25.00)	2021vs, 1953vs(b)	—	468 m/e (P <sup>+</sup> ) (Ni <sub>2</sub> Fe)	this work
(Cp) <sub>2</sub> Ni <sub>2</sub> Fe(CO) <sub>3</sub> (HC <sub>2</sub> Bu-t)	brown-green solid	49.00 (48.59)	4.38 (4.29)	11.34 (11.89)	10.65 (10.22)	24.63 (25.00)	2014 vs, 1951 vs, 1947vs(sh)	4.80s (5 H) 4.90s (5 H) 8.50s (9 H)	468 m/e (P <sup>+</sup> ) (Ni <sub>2</sub> Fe)	this work
(Cp)NiFe <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> Bu-t) (IVa)	grey-violet crystals	42.44 (42.13)	3.03 (2.91)	23.00 (23.04)	19.38 (19.81)	12.15 (12.11)	2056vs, 2014vs, 1981vs, 1966 s(sh)	4.80s (5 H) 8.00 s (9 H)	484 m/e (P <sup>+</sup> ) (NiFe <sub>2</sub> )	6
(Cp)NiFe <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> Me) (IVb)	grey-violet crystals	38.04 (37.95)	1.88 (1.82)	25.57 (25.25)	20.71 (21.69)	13.80 (33.26)	2060s, 2020vs, 1982s(sh), 1968m	4.80s (5 H) 7.94s (3 H)	422 m/e (P <sup>+</sup> ) (NiFe <sub>2</sub> )	3
(Cp)NiFe <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> Et) <sub>2</sub> (VI)	grey solid	42.03 (41.86)	3.16 (3.10)	23.41 (23.00)	19.02 (19.68)	12.38 (12.04)	2021vs, 1964 vs(b)	4.80s (5 H) 6.40-6.70 qq (4 H) 7.30-7.60 tt (6 H)	484 m/e (P <sup>+</sup> ) (NiFe <sub>2</sub> )	this work
(Cp)NiFe <sub>2</sub> (CO) <sub>7</sub> C·CH <sub>2</sub> CH <sub>3</sub> (Va)	grey-violet needles	38.04 (37.99)	1.88 (1.82)	25.57 (25.25)	20.71 (21.69)	13.80 (13.26)	2070s, 2036vs, 2012s, 1968m 1974m, 1745 m-w	4.85s (5 H) 5.75q (2 H) 8.25t (3 H)	472 m/e (P <sup>+</sup> ) (NiFe <sub>2</sub> )	3
(Cp)NiFe <sub>2</sub> (CO) <sub>7</sub> C·CH <sub>2</sub> ·CMe <sub>3</sub> (Vb)	brown solid	42.17 (42.00)	3.18 (3.13)	22.31 (21.70)	21.31 (21.76)	11.03 (11.41)	2068s, 2034vs 2005vs, 1997 s(sh), 1845m	—	514 m/e (P <sup>+</sup> ) (NiFe <sub>2</sub> )	this work

<sup>a</sup> In parenthesis composition of the isotopic pattern of P<sup>+</sup>. <sup>b</sup> 4.80s (10 H), 7.80s (9 H) We were not able to detect to alkynic H.

## SCHEME 1. REACTIONS AND REACTION CONDITIONS

Reactions of $(Cp)_2Ni$ with $Fe(CO)_5$	20 min, E <sup>a</sup>	$Ni(CO)_4$ , $[(Cp)Ni(CO)]_2$ , $[(Cp)Fe(CO)_2]_2$ (20%), $(Cp)_2NiFe(CO)_3$ , (tr)	[6]
with $Fe(CO)_5$	8 h, benzene	$(Cp)_2Ni_2Fe_2(CO)_7$ (10%)	[9]
with $Fe(CO)_4PPh_3$	30 min, E	$(Cp)_2NiFe(CO)_3$	[this work]
with $Fe_3(CO)_{12}$	20 min, E	$Ni(CO)_4$ , decomposition	[6]
with $Fe_3(CO)_{11}P(OEt)_3$	20 min, E	$Ni(CO)_4$ , $[(Cp)Fe(CO)_2]_2$ (20%), $(Cp)_2Ni_2Fe_2(CO)_7$ (10%)	[this work]
with $Fe_3(CO)_{10}P(OEt)_3$	20 min, 1/1, 5 <sup>b</sup>	$Ni(CO)_4$ , $[(Cp)Fe(CO)_2]_2$ (25%), $Fe(CO)_4P(OEt)_3$ (3%)	[this work]
with $Fe(CO)_9(C_2Et_2)$	20 min, E	$Ni(CO)_4$ , $[(Cp)Fe(CO)_2]_2$ (20%), $Fe(CO)_4P(OEt)_3$ (10%), $(Cp)_2Ni_2Fe_2(CO)_7$ (tr)	[this work]
Reactions of $[(Cp)Ni(CO)]_2$ with $Fe(CO)_5$	25 min, E	$Ni(CO)_4$ , $(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (20%), unidentified products (2)	[6]
with $Fe(CO)_4(PPh_3)$	20 min, E	$Ni(CO)_4$ , decomposition	[this work]
with $Fe(CO)_5 + C_2Ph_2$	22 h, benzene	$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ , $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ , $Fe_2(CO)_6(C_2Ph_2)$ (tr), $(Cp)_2Ni_2(C_2Ph_2)$ , $[(Cp)Fe(CO)_2]_2$	[9]
with $Fe_3(CO)_{12}$	25 min, E	$Ni(CO)_4$ , $[(Cp)Fe(CO)_2]_2$ (25%), $(Cp)_2Ni_2Fe_2(CO)_7$ (tr)	[6]
with $Fe_3(CO)_{11}P(OEt)_3$	20 min, E	$Ni(CO)_4$ , $[(Cp)_2Fe(CO)_2]_2$ (30%), $Fe(CO)_4P(OEt)_3$ (3%)	[this work]
with $Fe_3(CO)_9(C_2Et_2)$	40 min, E	$Ni(CO)_4$ , $(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ [20%]	[3]
with $Fe_3(CO)_9(C_2Ph_2)$	35 min, E	$Ni(CO)_4$ , $(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (30%), $Fe_2(CO)_6(C_2Ph_2)$ (30%) $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (10%), $(Cp)_2Ni_2Fe_2(CO)_7$ (tr), unidentified products (1)	[this work]

Reactions of $(Cp)_2Ni_2(CO)_2R'$ R = R' = Ph with $Fe(CO)_5$	25 min, 3/1 →	$Ni(CO)_4$ , $[(Cp)Fe(CO)]_2$ (10%), $Fe_2(CO)_6(C_2Ph_2)$ (2%), $Fe_2(CO)_9(C_2Ph_2)$ (2%), $(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (10%) $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (30%), unidentified products (3)	[this work]
with $Fe_3(CO)_{12}$	35 min, E →	$[(Cp)Fe(CO)]_2$ (10%), $Fe_3(CO)_9(C_2Ph_2)$ (2%), $Fe_2(CO)_6(C_2Ph_2)$ (2%) $Fe_3(CO)_8(C_2Ph_2)$ bridging CO's (3%), $(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (10%) $(Cp)_2Ni_2Fe_2(CO)_3(C_2Ph_2)$ (1-2%), unidentified products (6)	[this work]
R = R' = Et with $Fe(CO)_5$	25 min, 3/1 →	$[(Cp)Fe(CO)]_2$ (5%), $Fe_2(CO)_6(C_2Et_2)$ (10%), $Fe_2(CO)_5(C_2Et_2)_3CO$ (20%), $(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (10%), $(Cp)NiFe_2(CO)_6(C_2Et_2)$ (3%), unidentified products (3)	[this work]
with $Fe_3(CO)_{12}$	20 min, E →	$[(Cp)Fe(CO)]_2$ (3%), $Fe_3(CO)_9(C_2Et_2)$ (15%), $Fe_2(CO)_6(C_2Et_2)_2$ (5%), $Fe_3(CO)_8(C_2Et_2)_2$ bridging CO's (15%), $(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (20%), $(Cp)_2Ni_2Fe_2(CO)_7$ (tr), unidentified products (9)	[this work]
R = H, R' = <i>t</i> -Bu with $Fe(CO)_5$	30 min, 3/1 →	$[(Cp)Fe(CO)]_2$ (4%), $(Cp)_2Ni_2Fe_2(CO)_7$ (tr), $(Cp)_2Ni_2Fe_2(CO)_6(HC_2Bu-t)$ (tr), unidentified products (9)	[6]
with $Fe(CO)_{12}$	35 min, E →	$[(Cp)Fe(CO)]_2$ (10%), $(Cp)NiFe_2(CO)_6C_2Bu-t$ (6%) $(Cp)NiFe_2(CO)_7C_2H_2Bu-t$ (tr), $(Cp)_2Ni_2Fe(CO)_3(C_2H_2Bu-t)$ (tr) $(Cp)_2Ni_2Fe_2(CO)_6(HC_2Bu-t)$ (tr), unidentified products (13)	[6]
R = H, R' = Me with $Fe_3(CO)_{12}$	30 min, E →	$(Cp)_2Ni_2Fe_2(CO)_6(HC_2Me)$ (1%), $(Cp)NiFe_2(CO)_6(C_2Me)$ (15%), $(Cp)NiFe_2(CO)_7C_2H_2Me$ (5%)	[3]
R = H, R' = Ph with $Fe_3(CO)_{12}$	2 h, benzene →	$(Cp)_2Ni_2Fe_2(CO)_6(HC_2Ph)$ , $(Cp)_2Ni_2Fe(CO)_7(HC_2Ph)$ , $(Cp)_2Ni_2Fe(CO)_3(HC_2Ph)$ , $[(Cp)Fe(CO)]_2$ (12)	[9]
Reactions of $(Cp)_2Ni_2Fe_2(CO)_7$ with $C_2Et_2$	→	decomposition	

<sup>a</sup> E = equimolecular amounts of reactants, <sup>b</sup> Reactant ratio; the first figure refers to the nickel compound.

TABLE 2

FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) FOR THE NON-HYDROGEN ATOMS IN I (e.s.d.'s in parentheses)

	$x/a$	$y/b$	$z/c$
Fe(1)	3960(2)	2748(1)	888(2)
Fe(2)	940(2)	2118(1)	374(2)
Ni(1)	2774(1)	1870(1)	2964(1)
Ni(2)	1834(1)	3406(1)	2427(1)
O(1)	6150(10)	3358(6)	4058(11)
O(2)	5781(13)	3964(7)	-1080(14)
O(3)	5505(11)	1092(6)	-363(12)
O(4)	1662(11)	274(6)	-946(12)
O(5)	-1680(11)	2315(7)	-2449(12)
O(6)	-1514(10)	1770(6)	2713(11)
O(7)	1591(10)	3860(6)	-1157(10)
C(1)	5267(14)	3090(8)	2867(16)
C(2)	5076(16)	3484(9)	-316(17)
C(3)	4892(12)	1733(8)	133(14)
C(4)	1407(12)	1003(8)	-415(15)
C(5)	-658(15)	2237(9)	-1351(15)
C(6)	-511(13)	1903(7)	1823(14)
C(7)	1917(13)	3285(7)	-219(13)
C(8)	2692(16)	4679(8)	3782(15)
C(9)	1229(14)	4799(8)	2636(15)
C(10)	-114(15)	4240(8)	3054(15)
C(11)	519(17)	3765(9)	4487(16)
C(12)	2262(15)	4044(7)	4935(13)
C(13)	4676(23)	1164(13)	4341(26)
C(14)	3978(26)	1678(13)	5442(26)
C(15)	2367(23)	1455(10)	5370(17)
C(16)	1937(18)	707(10)	4090(20)
C(17)	3406(25)	522(10)	3397(20)

were taken from reference [16]. The function minimized in the least-squares calculations was  $\sum w|\Delta F|^2$ ; unit weights were chosen at each stage of the refinement after analyzing the variation of  $|\Delta F|$  with respect to  $|F_0|$ . Final atomic coordinates for non-hydrogen atoms are given in Table 2 for I and Table 3 for IIa, those of the hydrogen atoms in Table 4 for I and 5 for IIa; the thermal parameters of the non-hydrogen atoms are given in Table 6 for I and 7 for IIa. Lists of observed and calculated structure factors for both compounds are available from the authors on request.

All calculations were performed on the CYBER-76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna) with financial support from the University of Parma.

## Results and discussion

In absence of alkynes, ligand exchange between the metals predominates in the reactions; indeed, the formation of a nickel mirror in the reaction apparatus indicates that  $\text{Ni}(\text{CO})_4$  is formed and then decomposes during the reactions. This also accounts for the easy transfer of the cyclopentadienyl ligand, as shown by the frequent formation of  $(\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$  in substantial yield. By



TABLE 3

FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) FOR THE NON-HYDROGEN ATOMS IN IIa  
(e.s.d.'s in parentheses)

	$x/a$	$x/b$	$x/c$
Fe(1)	2533(2)	1703(2)	9371(3)
Fe(2)	1328(2)	3212(2)	6320(3)
Ni(1)	49(2)	2448(1)	7479(3)
Ni(2)	3352(2)	3033(1)	9011(3)
O(1)	1612(15)	70(9)	9797(19)
O(2)	5550(13)	882(9)	11601(18)
O(3)	1504(14)	3002(9)	11820(17)
O(4)	-1230(15)	3602(9)	3169(17)
O(5)	2828(14)	4219(9)	5010(17)
O(6)	99(14)	4817(9)	8181(17)
C(1)	1958(19)	714(13)	9613(22)
C(2)	4362(21)	1217(12)	10717(23)
C(3)	1904(18)	2498(12)	10805(23)
C(4)	-225(18)	3417(11)	4400(23)
C(5)	2247(18)	3812(11)	5527(22)
C(6)	608(19)	4179(15)	7503(21)
C(7)	3050(16)	1999(10)	7379(19)
C(8)	1666(16)	1776(10)	6751(21)
C(9)	1482(19)	904(11)	5556(21)
C(10)	569(26)	1162(15)	3643(24)
C(11)	4450(19)	1411(14)	6931(24)
C(12)	4468(24)	1638(15)	5244(27)
C(13)	3596(21)	4154(12)	10849(22)
C(14)	4698(19)	3286(13)	11579(21)
C(15)	5641(20)	2995(13)	10507(26)
C(16)	5054(18)	3715(13)	9192(26)
C(17)	3765(16)	4371(12)	9365(20)
C(18)	-1590(20)	3166(15)	8503(31)
C(19)	-1277(21)	2194(17)	8757(34)
C(20)	-1645(24)	1729(16)	7094(40)
C(21)	-2187(18)	2464(18)	5895(27)
C(22)	-2131(17)	3337(14)	6767(29)

TABLE 4

CALCULATED FRACTIONAL COORDINATES ( $\times 10^4$ ) FOR THE HYDROGEN ATOMS IN I

	$x/a$	$y/b$	$z/c$
H(8)	3916	5013	3776
H(9)	1153	5245	1611
H(10)	-1385	4182	2409
H(11)	-189	3283	5119
H(12)	3099	3811	5969
H(13)	5987	1209	4161
H(14)	4640	2220	6306
H(15)	1511	1781	6147
H(16)	718	357	3734
H(17)	3565	11	2377

TABLE 5  
CALCULATED FRACTIONAL COORDINATES ( $\times 10^4$ ) FOR THE HYDROGEN ATOMS IN IIa

	$x/a$	$y/b$	$z/c$
H(91)	939	507	6005
H(92)	2567	461	5641
H(101)	500	516	2917
H(102)	1100	1552	3160
H(103)	-528	1597	3524
H(111)	4512	664	6937
H(112)	5412	1544	7914
H(121)	5468	1198	5070
H(122)	4425	2380	5210
H(123)	3525	1500	4233
H(13)	2771	4570	11365
H(14)	4817	2917	12693
H(15)	6573	2373	10677
H(16)	5518	3750	8233
H(17)	3033	4946	8488
H(18)	-1437	3696	9492
H(19)	-834	1840	9982
H(20)	-1524	978	6845
H(21)	-2584	2380	4525
H(22)	-2459	4025	6170

TABLE 6  
THERMAL PARAMETERS ( $\times 10^4$ ) FOR THE NON-HYDROGEN ATOMS IN I (e.s.d.'s in parentheses).  
THEY ARE IN THE FORM:  $\exp[-2\pi^2(h^2a^*{}^2U_{11} + \dots + 2hka^*b^*U_{12})]$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Fe(1)	250(10)	330(10)	350(10)	50(10)	90(10)	40(10)
Fe(2)	270(10)	350(10)	310(10)	-10(10)	10(10)	19(10)
Ni(1)	380(10)	320(10)	300(10)	90(10)	40(10)	70(10)
Ni(2)	300(10)	280(10)	310(10)	10(10)	80(10)	60(10)
O(1)	430(40)	760(60)	650(50)	-170(40)	-110(40)	-80(40)
O(2)	1010(70)	1000(70)	1350(80)	560(60)	570(60)	-180(60)
O(3)	620(50)	590(50)	890(60)	-170(50)	160(50)	260(40)
O(4)	690(60)	460(50)	990(70)	-220(50)	110(50)	10(40)
O(5)	590(60)	1550(80)	700(60)	190(60)	-310(50)	50(50)
O(6)	410(50)	750(60)	710(50)	20(50)	260(40)	-30(40)
O(7)	620(50)	610(50)	480(50)	260(40)	70(40)	170(40)
C(1)	350(60)	400(70)	620(80)	10(60)	140(60)	60(50)
C(2)	490(70)	620(90)	720(90)	200(70)	260(60)	50(60)
C(3)	300(50)	610(70)	510(60)	10(50)	50(50)	50(50)
C(4)	370(50)	460(70)	510(70)	-30(60)	20(50)	-60(50)
C(5)	460(70)	770(90)	380(60)	50(60)	-20(50)	20(60)
C(6)	400(60)	430(60)	440(60)	-50(50)	30(50)	50(50)
C(7)	430(60)	450(60)	380(60)	110(50)	40(50)	100(50)
C(8)	560(80)	330(70)	490(60)	-100(50)	100(60)	-10(60)
C(9)	560(70)	330(60)	550(70)	-20(50)	180(50)	100(50)
C(10)	490(70)	440(70)	600(70)	-110(60)	200(60)	160(60)
C(11)	680(80)	450(80)	610(80)	-120(60)	410(70)	10(60)
C(12)	660(70)	490(60)	340(50)	-80(50)	40(50)	110(50)
C(13)	630(120)	1310(130)	1400(140)	1080(110)	230(100)	490(100)
C(14)	1310(150)	1140(140)	1250(150)	780(110)	-770(110)	-330(110)
C(15)	1720(140)	980(100)	540(70)	500(70)	610(80)	740(90)
C(16)	780(90)	800(80)	1140(110)	740(80)	-120(80)	-140(70)
C(17)	1910(150)	500(90)	750(100)	300(80)	330(100)	600(100)

TABLE 7

THERMAL PARAMETERS ( $\times 10^4$ ) FOR THE NON-HYDROGEN ATOMS IN IIa (e.s.d.'s in parentheses). THEY ARE IN THE FORM:  $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12})]$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Fe(1)	333(14)	282(13)	390(14)	16(12)	115(12)	-45(11)
Fe(2)	325(13)	371(14)	310(14)	17(12)	86(11)	-111(11)
Ni(1)	291(12)	392(13)	454(14)	53(11)	124(11)	-77(10)
Ni(2)	320(12)	349(13)	374(13)	-30(11)	96(11)	-121(9)
O(1)	901(107)	562(88)	1133(120)	21(82)	388(93)	-444(82)
O(2)	421(79)	561(85)	855(104)	187(75)	19(75)	-12(66)
O(3)	731(94)	611(88)	568(92)	-96(72)	323(77)	-121(72)
O(4)	617(91)	816(100)	570(89)	179(79)	-34(78)	-234(77)
O(5)	695(92)	741(95)	705(93)	62(76)	324(77)	-360(76)
O(6)	748(97)	527(89)	696(99)	-88(77)	359(81)	-31(74)
C(1)	515(114)	502(117)	515(115)	-247(95)	276(95)	-241(95)
C(2)	617(129)	339(99)	481(119)	-66(90)	246(105)	-54(91)
C(3)	382(105)	388(108)	552(110)	195(91)	141(89)	-22(83)
C(4)	368(97)	475(108)	471(114)	-27(91)	228(93)	-163(82)
C(5)	427(105)	372(97)	491(117)	-48(85)	174(91)	-21(82)
C(6)	413(109)	637(139)	286(100)	101(96)	14(84)	-274(102)
C(7)	373(94)	387(96)	360(94)	-51(77)	157(82)	-85(76)
C(8)	307(87)	260(87)	572(116)	26(81)	157(84)	-1(70)
C(9)	657(120)	424(105)	381(107)	-202(88)	145(91)	-157(89)
C(10)	1196(190)	780(146)	446(127)	8(110)	7(125)	-461(136)
C(11)	581(119)	876(145)	655(135)	-150(115)	499(109)	-259(107)
C(12)	960(167)	798(150)	689(148)	240(123)	411(134)	-68(125)
C(13)	798(136)	417(107)	397(112)	-78(90)	60(101)	-358(101)
C(14)	529(113)	653(130)	318(101)	-69(96)	69(93)	-310(101)
C(15)	554(122)	540(124)	783(145)	-152(118)	183(115)	-300(101)
C(16)	320(105)	661(129)	896(156)	-88(122)	82(104)	-434(98)
C(17)	280(100)	675(125)	283(99)	-28(91)	-105(79)	-252(90)
C(18)	419(117)	788(167)	941(181)	1(137)	457(124)	67(107)
C(19)	477(127)	830(172)	1101(209)	455(164)	461(137)	-72(121)
C(20)	573(143)	690(162)	1283(232)	-105(174)	349(154)	-217(122)
C(21)	212(98)	950(174)	768(156)	293(153)	-110(100)	-71(105)
C(22)	116(85)	699(145)	780(156)	162(124)	149(95)	28(84)

condensation of metal fragments,  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}_2(\text{CO})_7$  (I) is formed as a new product of these reactions. Despite the exchange processes, we have not until now been able to obtain heterometallic complexes bearing the cyclopentadienyl ligand on the iron atoms.

#### Complex I. Formation and structure

The synthesis of I is not selective, as the complex is obtained by treating nickelocene or bis(cyclopentadienylcarbonylnickel) with the iron carbonyls and also, in small amounts, in the reactions involving alkyne derivatives. Better yields are obtained when  $\text{Fe}_3(\text{CO})_{12}$  is used; thus, in our opinion, I originates from the "condensation" of  $\text{Fe}_2(\text{CO})_x$  fragments with  $(\eta\text{-C}_5\text{H}_5)\text{Ni}$  or  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2$ . Alternatively there may be substitution of a  $\text{Fe}(\text{CO})_5$  unit in the iron cluster followed by "condensation" of a second  $(\eta\text{-C}_5\text{H}_5)\text{Ni}$  fragment. The structure of complex I is represented in Fig. 1; bond distances and angles not involving hydrogen atoms are given in Table 8. This structure involves a tetrahedral  $\text{Fe}_2\text{-Ni}_2$  metal cluster, and six terminal CO's (one of which is slightly distorted)

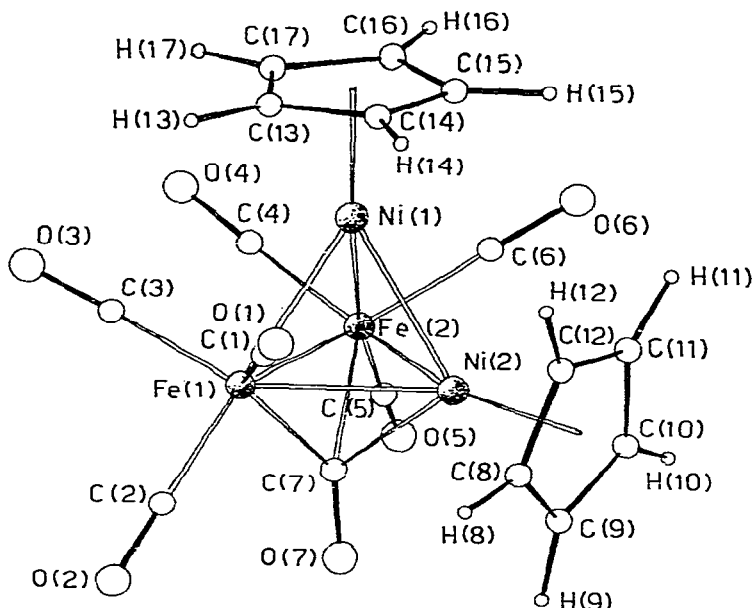


Fig. 1. View of the molecular shape of the complex  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}_2(\text{CO})_7$  (I) with the atomic numbering scheme.

are located three on each Fe atom, and the seventh CO triply bridges two Fe and one Ni atoms. Each Ni atom is  $\eta$ -bonded to a cyclopentadienyl ligand, the distance to the barycentre of the ring is 1.754 for Ni(1) and 1.725 Å for Ni(2).

Five metal–metal distances are very close (Fe(1)–Ni(1) 2.432(2), Fe(1)–Ni(2) 2.408(2), Fe(2)–Ni(1) 2.438(2), Fe(2)–Ni(2) 2.411(2) and Ni(1)–Ni(2) 2.441(2) Å) and the sixth one (Fe(1)–Fe(2) 2.530(2) Å) slightly longer. Both Ni–Ni and Fe–Fe distances are in the range of the shortest reported values [17]; thus in the other tetrahedral clusters 2.57–2.60 (for sides non-bridged by carbonyls) and 2.50 Å (for bridged sides) were found for  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  [18], a mean value of 2.520 Å for  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  [19] and 2.539 Å for  $(\eta\text{-C}_5\text{H}_5)_2\text{-Rh}_2\text{Fe}_2(\text{CO})_8$  [20].

Three CO's are coordinated to each iron as terminal ligands; however, the C(1)–O(1) is slightly bent towards Ni(1); the angle Fe(1)–C(1)–O(1) is 174.8° (against 177.0–179.8° for the other carbonyls) and the distance Ni(1)–C(1) is 2.637 Å. In iron clusters the following Fe–C distances and Fe–C–O angles have been found for very asymmetrically doubly bridging CO's: 2.489 Å, 164.1°; 2.705 Å, 169.3°; 2.586 Å, 169.0°; thus the above group can be considered as an "incipient semi-bridging" one [8].

The seventh CO is triply bridging between three metal atoms; similar behaviour has been found for cobalt [22] and iron [23] derivatives, but, to our knowledge, I is the first example of a similar feature involving different metals. The metal–carbon distances are: Fe(1)–C(7) 1.981(11), Fe(2)–C(7) 1.961(10) and Ni(2)–C(7) 2.110(10) Å and the angles around the apical C(7) are: Fe(1)–C(7)–Fe(2) 79.9(4), Fe(1)–C(7)–Ni(2) 72.1(3) and Fe(2)–C(7)–Ni(2) 72.6(4)°. These distances and angles are in the usual range for  $\sigma$  bonds in iron

TABLE 8

BOND DISTANCES (Å) AND ANGLES (°) NOT INVOLVING HYDROGEN ATOMS WITH e.s.d.'s IN PARENTHESES

(i) in the coordination sphere of the metals

Fe(1)—Fe(2)	2.530(2)	Fe(2)—C(7)	1.961(10)
Fe(1)—Ni(1)	2.432(2)	Ni(1)—C(13)	2.114(19)
Fe(1)—Ni(2)	2.408(2)	Ni(1)—C(14)	2.129(21)
Fe(2)—Ni(1)	2.438(2)	Ni(1)—C(15)	2.114(14)
Fe(2)—Ni(2)	2.411(2)	Ni(1)—C(16)	2.105(15)
Ni(1)—Ni(2)	2.441(2)	Ni(1)—C(17)	2.091(15)
Fe(1)—C(1)	1.802(12)	Ni(2)—C(7)	2.110(10)
Fe(1)—C(2)	1.782(13)	Ni(2)—C(8)	2.114(12)
Fe(1)—C(3)	1.779(11)	Ni(2)—C(9)	2.103(12)
Fe(1)—C(7)	1.981(11)	Ni(2)—C(10)	2.102(12)
Fe(2)—C(4)	1.765(12)	Ni(2)—C(11)	2.103(13)
Fe(2)—C(5)	1.781(12)	Ni(2)—C(12)	2.115(10)
Fe(2)—C(6)	1.776(11)		
Fe(2)—Fe(1)—Ni(1)	58.8(1)	C(13)—Ni(1)—C(14)	35.7(8)
Fe(2)—Fe(1)—Ni(2)	58.4(1)	C(13)—Ni(1)—C(15)	61.5(7)
Ni(1)—Fe(1)—Ni(2)	60.6(1)	C(13)—Ni(1)—C(16)	64.5(7)
Ni(1)—Fe(2)—Ni(2)	60.4(1)	C(13)—Ni(1)—C(17)	40.3(7)
Ni(1)—Fe(2)—Fe(1)	58.6(1)	C(13)—Ni(1)—Fe(1)	110.2(5)
Ni(2)—Fe(2)—Fe(1)	58.3(1)	C(13)—Ni(1)—Fe(2)	152.2(6)
Ni(2)—Ni(1)—Fe(1)	59.3(1)	C(14)—Ni(1)—C(15)	36.1(7)
Ni(2)—Ni(1)—Fe(2)	59.2(1)	C(14)—Ni(1)—C(16)	63.6(7)
Fe(1)—Ni(1)—Fe(2)	62.6(1)	C(14)—Ni(1)—C(17)	64.1(7)
Fe(1)—Ni(2)—Fe(2)	63.3(1)	C(14)—Ni(1)—Fe(1)	125.5(6)
Fe(1)—Ni(2)—Ni(1)	60.2(1)	C(14)—Ni(1)—Fe(2)	169.7(6)
Fe(2)—Ni(2)—Ni(1)	60.3(1)	C(15)—Ni(1)—C(16)	39.7(6)
Fe(2)—Fe(1)—C(1)	129.4(4)	C(15)—Ni(1)—C(17)	64.9(6)
Fe(2)—Fe(1)—C(2)	130.2(4)	C(15)—Ni(1)—Fe(1)	158.6(4)
Fe(2)—Fe(1)—C(3)	97.2(3)	C(15)—Ni(1)—Fe(2)	134.3(5)
Fe(2)—Fe(1)—C(7)	49.7(3)	C(16)—Ni(1)—C(17)	38.7(7)
Ni(1)—Fe(1)—C(1)	75.4(4)	C(16)—Ni(1)—Fe(1)	158.3(4)
Ni(1)—Fe(1)—C(2)	169.8(4)	C(16)—Ni(1)—Fe(2)	111.4(4)
Ni(1)—Fe(1)—C(3)	89.1(4)	C(17)—Ni(1)—Fe(1)	123.1(5)
Ni(1)—Fe(1)—C(7)	100.8(3)	C(17)—Ni(1)—Fe(2)	118.4(5)
Ni(2)—Fe(1)—C(1)	81.8(4)	C(7)—Ni(2)—C(8)	117.4(4)
Ni(2)—Fe(1)—C(2)	118.0(4)	C(7)—Ni(1)—C(9)	96.9(4)
Ni(2)—Fe(1)—C(3)	147.4(4)	C(7)—Ni(2)—C(10)	111.1(4)
Ni(2)—Fe(1)—C(7)	56.4(3)	C(7)—Ni(2)—C(11)	149.2(5)
C(1)—Fe(1)—C(2)	94.4(6)	C(7)—Ni(2)—C(12)	156.4(4)
C(1)—Fe(1)—C(3)	102.8(5)	C(7)—Ni(2)—Fe(1)	51.5(3)
C(1)—Fe(1)—C(7)	131.0(5)	C(7)—Ni(2)—Fe(2)	50.9(3)
C(2)—Fe(1)—C(3)	94.0(6)	C(7)—Ni(2)—Ni(1)	96.9(3)
C(2)—Fe(1)—C(7)	85.3(5)	C(8)—Ni(2)—C(9)	39.3(5)
C(3)—Fe(1)—C(7)	126.2(5)	C(8)—Ni(2)—C(10)	66.3(5)
Ni(1)—Fe(2)—C(4)	87.2(4)	C(8)—Ni(2)—C(11)	66.3(5)
Ni(1)—Fe(2)—C(5)	171.1(4)	C(8)—Ni(2)—C(12)	39.2(4)
Ni(1)—Fe(2)—C(6)	77.3(4)	C(8)—Ni(2)—Fe(1)	111.7(4)
Ni(1)—Fe(2)—C(7)	101.2(3)	C(8)—Ni(2)—Fe(2)	168.2(3)
Ni(2)—Fe(2)—C(4)	145.3(4)	C(8)—Ni(2)—Ni(1)	127.9(3)
Ni(2)—Fe(2)—C(5)	120.5(4)	C(9)—Ni(2)—C(10)	39.3(5)
Ni(2)—Fe(2)—C(6)	82.5(4)	C(9)—Ni(2)—C(11)	66.1(5)
Ni(2)—Fe(2)—C(7)	56.6(3)	C(9)—Ni(2)—C(12)	65.9(4)
C(4)—Fe(2)—C(5)	93.5(6)	C(9)—Ni(2)—Fe(1)	126.7(3)
C(4)—Fe(2)—C(6)	103.6(5)	C(9)—Ni(2)—Fe(2)	133.7(3)
C(4)—Fe(2)—C(7)	126.0(5)	C(9)—Ni(2)—Ni(1)	165.3(3)
C(4)—Fe(2)—Fe(1)	95.5(3)	C(10)—Ni(2)—C(11)	39.8(5)
C(5)—Fe(2)—C(6)	93.9(5)	C(10)—Ni(2)—C(12)	66.5(5)
C(5)—Fe(2)—C(7)	85.6(5)	C(10)—Ni(2)—Fe(1)	160.6(3)

TABLE 8 (continued)

C(5)—Fe(2)—Fe(1)	130.1(4)	C(10)—Ni(2)—Fe(2)	114.4(3)
C(6)—Fe(2)—C(7)	130.4(5)	C(10)—Ni(2)—Ni(1)	137.3(3)
C(6)—Fe(2)—Fe(1)	130.8(4)	C(11)—Ni(2)—C(12)	39.8(5)
C(7)—Fe(2)—Fe(1)	50.4(3)	C(11)—Ni(2)—Fe(1)	159.0(4)
Ni(2)—Ni(1)—C(13)	143.1(5)	C(11)—Ni(2)—Fe(2)	122.5(4)
Ni(2)—Ni(1)—C(14)	117.7(5)	C(11)—Ni(2)—Ni(1)	103.5(4)
Ni(2)—Ni(1)—C(15)	114.2(4)	C(12)—Ni(2)—Fe(1)	125.2(3)
Ni(2)—Ni(1)—C(16)	138.1(4)	C(12)—Ni(2)—Fe(2)	152.6(3)
Ni(2)—Ni(1)—C(17)	176.1(5)	C(12)—Ni(2)—Ni(1)	99.4(3)
<i>(ii) in the carbonyl groups</i>			
O(1)—C(1)	1.142(15)	O(5)—C(5)	1.137(15)
O(2)—C(2)	1.141(17)	O(6)—C(6)	1.158(14)
O(3)—C(3)	1.138(14)	O(7)—C(7)	1.181(13)
O(4)—C(4)	1.147(15)		
Fe(1)—C(1)—O(1)	174.8(1.1)	Fe(1)—C(7)—Fe(2)	79.9(4)
Fe(1)—C(2)—O(2)	179.2(1.2)	Fe(1)—C(7)—Ni(2)	72.1(3)
Fe(1)—C(3)—O(3)	178.9(1.0)	Fe(1)—C(7)—O(7)	137.5(9)
Fe(2)—C(4)—O(4)	178.0(9)	Fe(2)—C(7)—Ni(2)	72.6(4)
Fe(2)—C(5)—O(5)	179.8(1.1)	Fe(2)—C(7)—O(7)	139.2(9)
Fe(2)—C(6)—O(6)	177.0(1.0)	Ni(2)—C(7)—O(7)	126.2(8)
<i>(iii) in the organic ligands</i>			
C(8)—C(9)	1.419(17)	C(13)—C(14)	1.302(28)
C(8)—C(12)	1.417(16)	C(13)—C(17)	1.449(26)
C(9)—C(10)	1.415(17)	C(14)—C(15)	1.314(28)
C(10)—C(11)	1.430(17)	C(15)—C(16)	1.431(21)
C(11)—C(12)	1.434(18)	C(16)—C(17)	1.390(24)
C(9)—C(8)—C(12)	107.9(1.1)	C(14)—C(13)—C(17)	108.8(1.7)
C(9)—C(8)—Ni(2)	69.9(7)	C(14)—C(13)—Ni(1)	72.8(1.2)
C(12)—C(8)—Ni(2)	70.5(6)	C(17)—C(13)—Ni(1)	69.0(1.0)
C(10)—C(9)—Ni(2)	70.3(7)	C(15)—C(14)—Ni(1)	71.3(1.1)
C(10)—C(9)—C(8)	108.9(1.0)	C(15)—C(14)—C(13)	111.5(1.8)
Ni(2)—C(9)—C(8)	70.8(7)	Ni(1)—C(14)—C(13)	71.5(1.3)
C(11)—C(10)—Ni(2)	70.1(7)	C(16)—C(15)—Ni(1)	69.8(8)
C(11)—C(10)—C(9)	107.5(1.1)	C(16)—C(15)—C(14)	108.6(1.5)
Ni(2)—C(10)—C(9)	70.4(7)	Ni(1)—C(15)—C(14)	72.6(1.1)
C(12)—C(11)—Ni(2)	70.6(7)	C(17)—C(16)—Ni(1)	70.1(9)
C(12)—C(11)—C(10)	107.7(1.1)	C(17)—C(16)—C(15)	106.1(1.4)
Ni(2)—C(11)—C(10)	70.1(7)	Ni(1)—C(16)—C(15)	70.5(8)
Ni(2)—C(12)—C(8)	70.4(6)	Ni(1)—C(17)—C(13)	70.7(1.0)
Ni(2)—C(12)—C(11)	69.7(7)	Ni(1)—C(17)—C(16)	71.2(9)
C(8)—C(12)—C(11)	107.9(1.0)	C(13)—C(17)—C(16)	105.0(1.4)

and cobalt complexes [24] containing apical C—R and CO groups; the longer Ni—C distance and the narrower Fe—C—Ni angles make this apical group considerably distorted. Indeed, on the basis of the E.A.N. rule, this carbonyl should bridge the iron atoms only; thus the behaviour of Ni(2) is not in accord with the E.A.N. formalism, as it is bound to a cyclopentadienyl group and four other atoms.

A tetradentate nature of the ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ni group has been observed previously in two other cases [5,6]; this behaviour is probably due to the good electron donor properties of this group, which appears to be a valuable “building block”

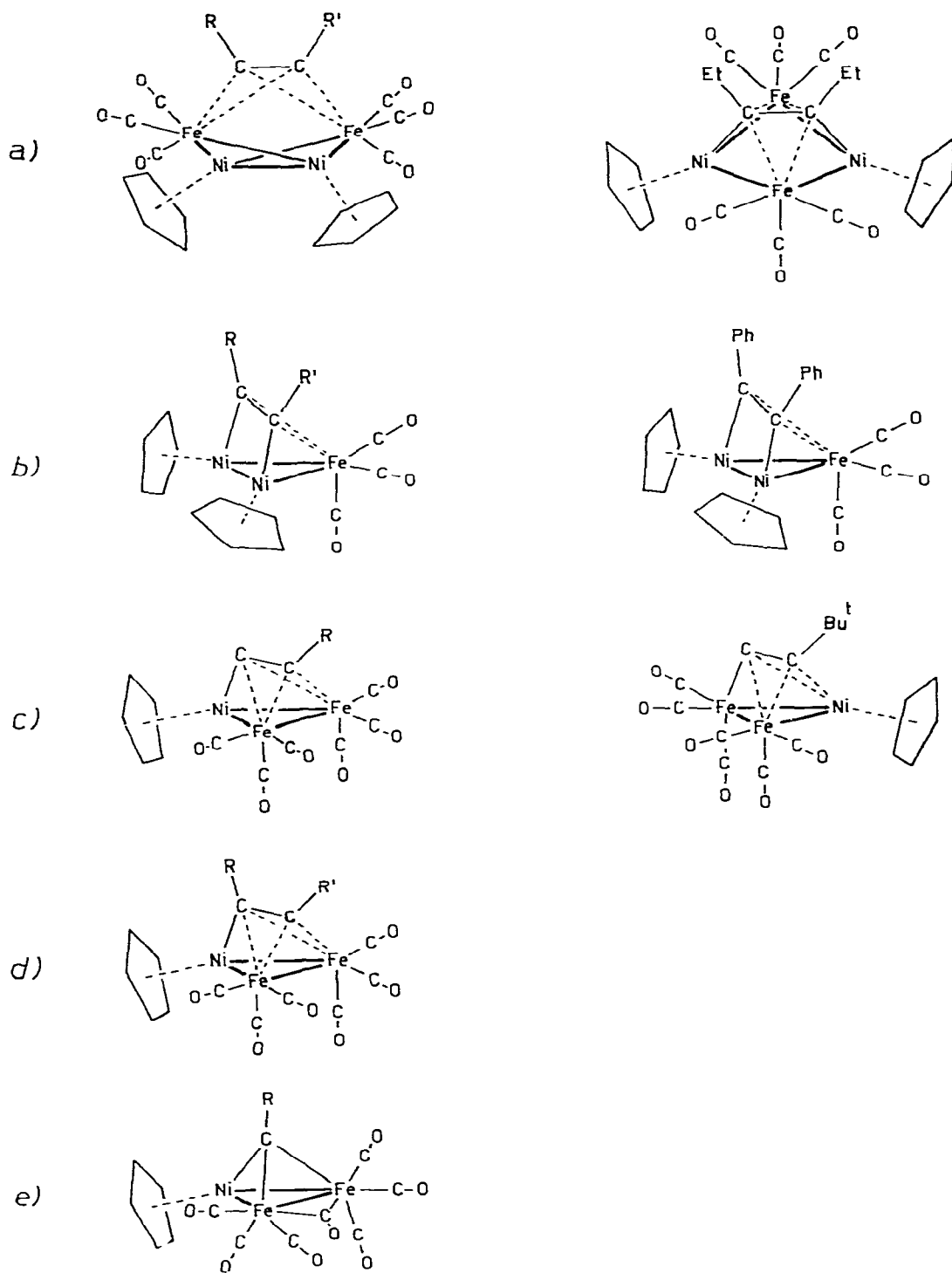


Fig. 2. Left column: proposed structures (a) for II [3], (b) for III [9], (c) for IV [3], (d) for VI and (e) for V [3]. Right column: determined structures (a) for IIa, (b) for IIIa [31], (c) for IVa [6].

for the synthesis of new clusters. The synthesis of I also indicates that in absence of alkynes the preferred metal atom arrangement is tetrahedral.

### *Heterometallic alkyne derivatives*

In the presence of alkynes a considerable number of derivatives, some of which still under investigation, are formed: the tetranuclear derivatives  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}_2(\text{CO})_6(\text{RC}_2\text{R}')$  ( $\text{R} = \text{R}' = \text{Et}$ , complex IIa;  $\text{R} = \text{R}' = \text{Ph}$ , IIb;  $\text{R} = \text{H}$ ,  $\text{R}' = \text{Me}$ , IIc;  $\text{R} = \text{H}$ ,  $\text{R}' = \text{t-Bu}$ , IId), the trinuclear derivatives  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{-Fe}(\text{CO})_3(\text{RC}_2\text{R}')$  ( $\text{R} = \text{R}' = \text{Ph}$ , IIIa;  $\text{R} = \text{R}' = \text{Et}$ , IIIb;  $\text{R} = \text{H}$ ,  $\text{R}' = \text{t-Bu}$ , IIIc),  $(\eta\text{-C}_5\text{H}_5)\text{NiFe}_2(\text{CO})_6\text{C}_2\text{R}$  ( $\text{R} = \text{t-Bu}$ , IVa;  $\text{R} = \text{Me}$ , IVb),  $(\eta\text{-C}_5\text{H}_5)\text{NiFe}_2(\text{CO})_6\text{-}(\text{RC}_2\text{R}')$  ( $\text{R} = \text{R}' = \text{Et}$ , VI) and finally  $(\eta\text{-C}_5\text{H}_5)\text{NiFe}_2(\text{CO})_7\text{CCH}_2\text{R}$  ( $\text{R} = \text{Me}$ , Va;  $\text{R} = \text{t-Bu}$ , Vb). The structures proposed for these derivatives on the basis of spectroscopic results and those determined for IIa, IIIa and IVa are presented in Fig. 2.

Alkyne exchange is also observed: the  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{RC}_2\text{R}')$  complexes show considerable tendency to release alkyne, as can be inferred from the formation of homometallic alkynyliron (bi- and tri-nuclear) derivatives, sometimes in high yields.

### *Complex IIa and homologues. Formation and structures*

The formation of the complexes II is not selective; they can be obtained either from  $\text{HC}_2\text{R}$  and  $\text{RC}_2\text{R}$  alkynes, from nickelocene or bis(cyclopentadienylcarbonylnickel) and alkynyliron clusters, and from  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{RC}_2\text{R}')$  complexes and iron carbonyls. Better yields are obtained when  $\text{Fe}_3(\text{CO})_9\text{RC}_2\text{R}$  derivatives ( $\text{R} = \text{Ph}$ , Et) are brought into reaction with cyclopentadienylnickel derivatives; this is probably due to the presence of existing  $\text{Fe}-\text{C}(\pi)$  bonds, and to the possible formation of  $\text{Fe}_2(\text{CO})_6\text{RC}_2\text{R}$  intermediates by loss of the  $\sigma$ -bonded  $\text{Fe}(\text{CO})_3$  fragment, as inferred from the mass spectral data [25]. Lower yields are obtained from alkynylcyclopentadienylnickel derivatives and iron carbonyls; this can be explained by assuming that easy alkyne release and transfer to yield homometallic iron complexes competes with the formation of heterometallic clusters. We were not able to isolate products derived from alkyne isomerisation from either the reactions giving heterometallic clusters, or those giving homometallic alkyne derivatives. The alkyne  $\text{C}_2\text{Et}_2$  has been shown to undergo isomerisation readily in the presence of ruthenium carbonyl clusters [26]. All the obtained tetra- and tri-metallic iron derivatives contain non-isomerized hex-3-yne.

The formation of  $\text{Fe}_2\text{Ni}_2$  clusters is in accord with the well known tendency of the iron carbonyl and alkynylcarbonyl clusters to undergo decomposition; on the other hand, from ruthenium clusters, only  $\text{Ru}_3\text{Ni}$  derivatives had previously been obtained [4,5].

The structure of complex IIa is represented in Fig. 3; bond distances and angles not involving hydrogen atoms are given in Table 9. The structure is characterized by a tetranuclear cluster of two Fe and two Ni atoms coordinated by six terminal carbonyls (through the Fe atoms), by two cyclopentadienyl ligands (through the Ni atoms) and by one  $\sigma$ - and  $\pi$ -bonded hex-3-yne molecule (through all the metal atoms). The Fe and Ni atoms of the cluster alternate at the vertices of a tetrahedrally distorted square. Fe(1), Ni(1), Fe(2) and Ni(2) are 0.26, -0.27, 0.30 and -0.29 Å out of the mean least-squares plane passing



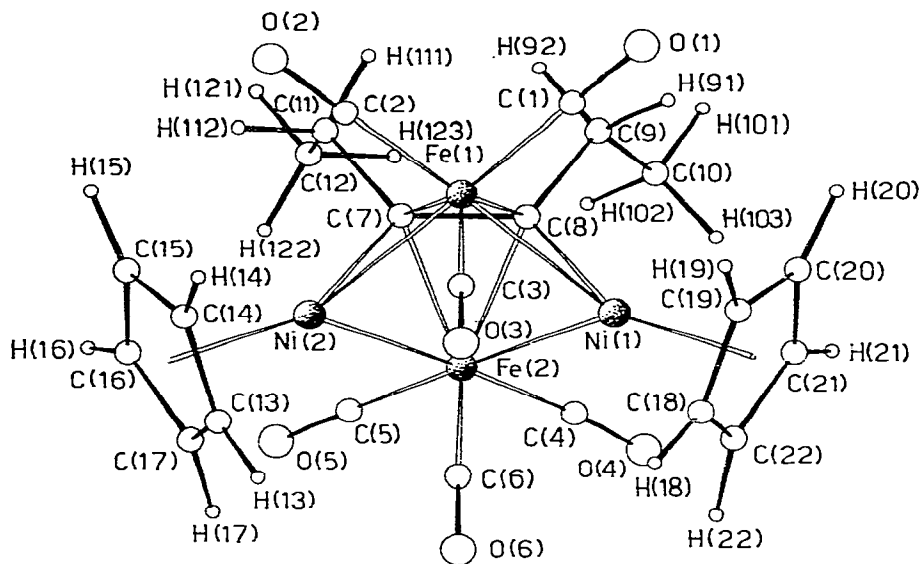


Fig. 3. View of the molecular shape of the complex  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Et}_2)$  (IIa) with the atomic numbering scheme.

through them. The metal–metal bond distances are: Fe(1)–Ni(1) 2.426(3), Ni(1)–Fe(2) 2.422(3), Fe(2)–Ni(2) 2.414(3) and Ni(2)–Fe(1) 2.417(3) Å; the Fe(1)–Fe(2) and Ni(1)–Ni(2) non-bonding distances being 3.204 and 3.454 Å respectively. The Fe–Ni bonds in IIa agree well with those found in I. Tetrametallic clusters with only four metal–metal interactions are relatively rare [21a,27]; one alkynyliridium carbonyl derivative has been reported [28] which is well comparable with IIa. This latter, however, is the first example of a square heterometallic alkyne derivative. Attempts to obtain IIa by treating I with  $\text{EtC}_2\text{Et}$  under various sets of reaction conditions led only to extensive decomposition. Thus we consider that IIa is not formed by simple tetrahedral cluster opening (like that of  $\text{Co}_4(\text{CO})_{10}\text{C}_2\text{Et}_2$  from  $\text{Co}_4(\text{CO})_{12}$  [29]): the reaction scheme proposed above, involving  $\text{Fe}_2(\text{CO})_6\text{C}_2\text{Et}_2$  fragments, is supported by this evidence.

Each Fe atom is bound to three terminal CO's (as shown by the Fe–C–O angles ranging from 176.2 to 178.8°). Each Ni atom is  $\eta$  bonded to a cyclopentadienyl ligand, the distance to the barycentre of the ring being 1.768 for Ni(1) and 1.774 Å for Ni(2).

The alkyne is bonded to the Ni atoms through  $\sigma$ -bonds (Ni(1)–C(8) 1.918(17) and Ni(2)–C(7) 1.955(15) Å) and to the Fe atoms through  $\pi$  bonds (Fe(1)–C(7) 2.043(16), Fe(1)–C(8) 2.054(17), Fe(2)–C(7) 2.091(16) and Fe(2)–C(8) 2.081(16) Å). The alkyne carbon atoms C(9), C(8), C(7) and C(11) are perfectly coplanar, but Ni(1) and Ni(2) atoms are 0.15 and 0.13 Å out of the plane passing through them. The C(7)–C(8) bond (1.431(23) Å) is in the range of the values found for  $\mu_4\text{-}\eta^2$  alkynes [10,21]. In this complex the E.A.N. formalism is satisfied since each Ni atom is bonded to one cyclopentadienyl ligand, to two Fe atoms and  $\sigma$  to one alkyne carbon, whereas each Fe atom is bonded to three CO's, to two Ni atoms and interacts  $\pi$  with the alkyne. In this

TABLE 9

BOND DISTANCES (Å) AND ANGLES (°) (NOT INVOLVING HYDROGEN ATOMS) WITH *e.s.d.*'s*(i) in the coordination sphere of the metals*

Fe(1)—Ni(1)	2.426(3)	Fe(2)—C(8)	2.081(16)
Fe(1)—Ni(2)	2.417(3)	Ni(1)—C(8)	1.918(17)
Fe(2)—Ni(1)	2.422(3)	Ni(1)—C(18)	2.103(22)
Fe(2)—Ni(2)	2.414(3)	Ni(1)—C(19)	2.124(24)
Fe(1)—C(1)	1.769(20)	Ni(1)—C(20)	2.180(26)
Fe(1)—C(2)	1.757(20)	Ni(1)—C(21)	2.166(20)
Fe(1)—C(3)	1.746(19)	Ni(1)—C(22)	2.107(19)
Fe(1)—C(7)	2.043(16)	Ni(2)—C(7)	1.955(15)
Fe(1)—C(8)	2.054(17)	Ni(2)—C(13)	2.145(18)
Fe(2)—C(4)	1.774(18)	Ni(2)—C(14)	2.157(17)
Fe(2)—C(5)	1.770(18)	Ni(2)—C(15)	2.187(21)
Fe(2)—C(6)	1.778(20)	Ni(2)—C(16)	2.188(20)
Fe(2)—C(7)	2.091(16)	Ni(2)—C(17)	2.096(18)
Ni(1)—Fe(1)—Ni(2)	91.0(1)	C(8)—Ni(1)—Fe(1)	54.9(5)
Ni(1)—Fe(2)—Ni(2)	91.2(1)	C(8)—Ni(1)—Fe(2)	55.9(5)
Fe(1)—Ni(1)—Fe(2)	82.7(1)	C(18)—Ni(1)—C(19)	38.4(9)
Fe(1)—Ni(2)—Fe(2)	83.0(1)	C(18)—Ni(1)—C(20)	65.5(9)
Ni(1)—Fe(1)—C(1)	89.5(6)	C(18)—Ni(1)—C(21)	64.4(9)
Ni(1)—Fe(1)—C(2)	176.8(6)	C(18)—Ni(1)—C(22)	38.3(9)
Ni(1)—Fe(1)—C(3)	80.8(6)	C(18)—Ni(1)—Fe(1)	120.0(7)
Ni(1)—Fe(1)—C(7)	81.9(5)	C(18)—Ni(1)—Fe(2)	125.1(6)
Ni(1)—Fe(1)—C(8)	49.9(5)	C(19)—Ni(1)—C(20)	39.7(1.1)
Ni(2)—Fe(1)—C(1)	178.8(6)	C(19)—Ni(1)—C(21)	63.9(9)
Ni(2)—Fe(1)—C(2)	85.8(6)	C(19)—Ni(1)—C(22)	64.0(9)
Ni(2)—Fe(1)—C(3)	80.7(6)	C(19)—Ni(1)—Fe(1)	102.7(8)
Ni(2)—Fe(1)—C(7)	51.2(4)	C(19)—Ni(1)—Fe(2)	163.0(7)
Ni(2)—Fe(1)—C(8)	82.3(5)	C(20)—Ni(1)—C(21)	37.5(1.0)
C(1)—Fe(1)—C(2)	93.7(9)	C(20)—Ni(1)—C(22)	64.5(9)
C(1)—Fe(1)—C(3)	100.3(9)	C(20)—Ni(1)—Fe(1)	118.1(7)
C(1)—Fe(1)—C(7)	127.9(7)	C(20)—Ni(1)—Fe(2)	150.1(8)
C(1)—Fe(1)—C(8)	97.3(7)	C(21)—Ni(1)—C(22)	38.7(9)
C(2)—Fe(1)—C(3)	98.9(9)	C(21)—Ni(1)—Fe(1)	154.1(7)
C(2)—Fe(2)—C(7)	95.9(8)	C(21)—Ni(1)—Fe(2)	116.9(6)
C(2)—Fe(1)—C(8)	129.3(8)	C(22)—Ni(1)—Fe(1)	157.3(6)
C(3)—Fe(1)—C(7)	128.3(8)	C(22)—Ni(1)—Fe(2)	105.3(6)
C(3)—Fe(1)—C(8)	127.1(8)	C(7)—Ni(2)—C(13)	176.9(7)
C(7)—Fe(1)—C(8)	40.9(6)	C(7)—Ni(2)—C(14)	141.0(7)
Ni(1)—Fe(2)—C(4)	88.4(6)	C(7)—Ni(2)—C(15)	116.4(7)
Ni(1)—Fe(2)—C(5)	177.6(6)	C(7)—Ni(2)—C(16)	119.1(7)
Ni(1)—Fe(2)—C(6)	80.5(7)	C(7)—Ni(2)—C(17)	144.1(6)
Ni(1)—Fe(2)—C(7)	81.1(5)	C(7)—Ni(2)—Fe(1)	54.5(5)
Ni(1)—Fe(2)—C(8)	49.7(5)	C(7)—Ni(2)—Fe(2)	56.0(5)
Ni(2)—Fe(2)—C(4)	176.0(6)	C(13)—Ni(2)—C(14)	39.1(7)
Ni(2)—Fe(2)—C(5)	88.1(6)	C(13)—Ni(2)—C(15)	65.7(8)
Ni(2)—Fe(2)—C(6)	78.6(6)	C(13)—Ni(2)—C(16)	64.0(8)
Ni(2)—Fe(2)—C(7)	50.8(4)	C(13)—Ni(2)—C(17)	38.4(7)
Ni(2)—Fe(2)—C(8)	81.8(5)	C(13)—Ni(2)—Fe(1)	122.7(5)
C(4)—Fe(2)—C(5)	92.2(8)	C(13)—Ni(2)—Fe(2)	123.5(5)
C(4)—Fe(2)—C(6)	97.4(8)	C(14)—Ni(2)—C(15)	40.0(7)
C(4)—Fe(2)—C(7)	132.9(7)	C(14)—Ni(2)—C(16)	65.0(7)
C(4)—Fe(2)—C(8)	100.9(7)	C(14)—Ni(2)—C(17)	65.7(7)
C(5)—Fe(2)—C(6)	97.2(9)	C(14)—Ni(2)—Fe(1)	102.9(5)
C(5)—Fe(2)—C(7)	100.1(7)	C(14)—Ni(2)—Fe(2)	161.8(5)
C(5)—Fe(2)—C(8)	132.3(8)	C(15)—Ni(2)—C(16)	38.5(8)
C(6)—Fe(2)—C(7)	125.2(7)	C(15)—Ni(2)—C(17)	65.8(7)
C(6)—Fe(2)—C(8)	125.6(8)	C(15)—Ni(2)—Fe(1)	116.7(5)
C(7)—Fe(2)—C(8)	40.1(6)	C(15)—Ni(2)—Fe(2)	150.8(6)
C(8)—Ni(2)—C(18)	174.9(8)	C(16)—Ni(2)—C(17)	38.7(7)
C(8)—Ni(1)—C(19)	140.1(8)	C(16)—Ni(2)—Fe(1)	153.0(5)
C(8)—Ni(1)—C(20)	116.5(8)	C(16)—Ni(2)—Fe(2)	116.3(5)
C(8)—Ni(1)—C(21)	120.2(8)	C(17)—Ni(2)—Fe(1)	160.2(5)
C(8)—Ni(1)—C(22)	146.7(8)	C(17)—Ni(2)—Fe(2)	103.3(5)

TABLE 9 (continued)

<i>(ii) in the carbonyl groups</i>			
O(1)—C(1)	1.142(25)	O(4)—C(4)	1.145(23)
O(2)—C(2)	1.149(24)	O(5)—C(5)	1.155(23)
O(3)—C(3)	1.176(23)	O(6)—C(6)	1.134(25)
Fe(1)—C(1)—O(1)	178.6(1.7)	Fe(2)—C(4)—O(4)	176.2(1.6)
Fe(1)—C(2)—O(2)	178.5(1.7)	Fe(2)—C(5)—O(5)	178.8(1.6)
Fe(1)—C(3)—O(3)	177.2(1.0)	Fe(2)—C(6)—O(6)	176.5(1.6)
<i>(iii) in the organic ligands</i>			
C(7)—C(8)	1.431(23)	C(15)—C(16)	1.442(29)
C(7)—C(11)	1.580(26)	C(16)—C(17)	1.422(26)
C(8)—C(9)	1.557(23)	C(18)—C(19)	1.388(35)
C(9)—C(10)	1.556(26)	C(18)—C(22)	1.380(33)
C(11)—C(12)	1.495(29)	C(19)—C(20)	1.461(40)
C(13)—C(14)	1.439(27)	C(20)—C(21)	1.396(37)
C(13)—C(17)	1.396(24)	C(21)—C(22)	1.416(34)
C(14)—C(15)	1.486(28)		
Fe(1)—C(7)—Fe(2)	101.5(7)	C(15)—C(14)—C(13)	106.9(1.6)
Fe(1)—C(7)—Ni(2)	74.4(5)	Ni(2)—C(14)—C(13)	70.0(1.0)
Fe(2)—C(7)—Ni(2)	73.2(5)	C(16)—C(15)—Ni(2)	70.8(1.1)
C(8)—C(7)—C(11)	124.0(1.4)	C(16)—C(15)—C(14)	105.8(1.7)
C(8)—C(7)—Fe(1)	69.9(9)	Ni(2)—C(15)—C(14)	68.9(1.0)
C(8)—C(7)—Fe(2)	69.6(9)	C(17)—C(16)—Ni(2)	67.2(1.0)
C(8)—C(7)—Ni(1)	33.4(8)	C(17)—C(16)—C(15)	108.8(1.7)
C(8)—C(7)—Ni(2)	120.6(1.2)	Ni(2)—C(16)—C(15)	70.7(1.1)
C(11)—C(7)—Fe(1)	124.8(1.1)	Ni(2)—C(17)—C(16)	74.2(1.1)
C(11)—C(7)—Fe(2)	133.6(1.2)	Ni(2)—C(17)—C(13)	72.7(1.1)
C(11)—C(7)—Ni(2)	115.3(1.2)	C(13)—C(17)—C(16)	109.2(1.6)
Fe(1)—C(8)—Fe(2)	101.5(7)	C(19)—C(18)—Ni(1)	71.6(1.3)
Fe(1)—C(8)—Ni(1)	75.2(7)	C(22)—C(18)—Ni(1)	71.0(1.2)
Fe(2)—C(8)—Ni(1)	74.4(6)	C(19)—C(18)—C(22)	108.1(2.1)
C(9)—C(8)—Fe(1)	124.7(1.1)	C(20)—C(19)—C(18)	108.8(2.3)
C(9)—C(8)—Fe(2)	133.7(1.2)	Ni(1)—C(19)—C(18)	70.0(1.4)
C(9)—C(8)—Ni(1)	117.6(1.2)	C(20)—C(19)—Ni(1)	72.3(1.4)
C(9)—C(8)—C(7)	119.8(1.5)	C(21)—C(20)—C(19)	105.2(2.1)
Fe(1)—C(8)—C(7)	69.2(9)	Ni(1)—C(20)—C(19)	68.1(1.4)
Fe(2)—C(8)—C(7)	70.3(9)	C(21)—C(20)—Ni(1)	70.7(1.4)
Ni(1)—C(8)—C(7)	122.4(1.2)	C(22)—C(21)—C(20)	108.9(2.0)
C(10)—C(9)—C(8)	114.7(1.5)	Ni(1)—C(21)—C(20)	71.8(1.4)
C(12)—C(11)—C(7)	115.7(1.7)	Ni(1)—C(21)—C(22)	68.4(1.2)
C(14)—C(13)—C(17)	109.0(1.7)	Ni(1)—C(22)—C(21)	72.9(1.1)
C(14)—C(13)—Ni(2)	70.9(1.0)	Ni(1)—C(22)—C(18)	70.7(1.2)
C(17)—C(13)—Ni(2)	68.9(1.0)	C(18)—C(22)—C(21)	108.9(2.0)
C(15)—C(14)—Ni(2)	71.1(1.0)		

complex the alkyne, a formal six electron donor, acts, as previously discussed for other heterometallic derivatives [6], to balance the electronic differences among heterometals and hence to stabilize the cluster in the same way as the semibridging CO's [30].

#### *Trinuclear heterometallic derivatives*

Some of these derivatives, namely the complexes IVb and Va were reported previously [3], as was complex IIIa [9]. Their structures were proposed on the basis of spectroscopic data but some doubt remains. A recent X-ray study on

complex IVa [6] has shown that the structure proposed on the E.A.N. basis was incorrect (see Fig. 2). The determination of the structure of IIIa is in progress [31]. We have not yet been able to obtain crystals of V suitable for X-ray analysis.

In the above reactions some indications were obtained of the factors influencing the type and yield of the heterotrimetallic complexes. Thus high yields of  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_3(\text{C}_2\text{Ph}_2)$  are obtained by treating  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{C}_2\text{Ph}_2)$  with iron carbonyls, but the reactions of  $\text{Fe}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)$  with nickelocene and bis(cyclopentadienylcarbonylnickel) give only traces of this product. This strongly points to the formation of IIIa through addition of "iron fragments" to  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{C}_2\text{Ph}_2)$ .

On the other hand, the nature of the alkyne seems to be the determining factor for the formation of some structures; thus from  $\text{HC}_2\text{R}$  alkynes (R = Me, t-Bu) complexes IV and V can be obtained from the same reaction, probably via intramolecular hydrogen exchange [3]. However, from  $\text{EtC}_2\text{Et}$ , the complex  $(\eta\text{-C}_5\text{H}_5)\text{NiFe}_2(\text{CO})_6(\text{C}_2\text{Et}_2)$  (VI) is obtained; it shows high symmetry in the IR spectrum, and its structure is probably similar to that found for IVa (see Fig. 2).

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